Progress in Organic Coatings 85 (2015) 15–21

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Development of novel anisotropic Janus composite particles based on Urushiol-iron/polystyrene polymer

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ARTICLE INFO

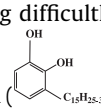
Article history:
Received 11 June 2014
Received in revised form
16 September 2014
Accepted 19 September 2014
Available online 19 March 2015

Keywords:
Renewable resources
Raw lacquer
Urushiol
Core–shell
Janus particles

ABSTRACT

The main component of raw lacquer is urushiol (U) which can react with metal compounds. In this paper, we focused on the application of raw lacquer in the synthesis of anisotropic Janus composite particles based on urushiol-iron/polystyrene polymer. The surface of polystyrene (PS) microspheres formed rich sulfonic groups after being sulfonated with concentrated sulfuric acid, which easily absorb Fe^{3+}. Urushiol reacted with Fe^{3+} forming the urushiol-iron (UFe) coordination compound, and then generated UFe/PS core–shell composite microspheres. After swelling polymerization with 2-propenoic acid, 2-methyl-, 3-(trimethoxysilyl) propyl ester (MPS), the asymmetric Janus composite particles of UFe–PMPS were obtained. Scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), transmission electron microscopy (TEM), infrared spectroscopy (IR), thermal gravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) were used to explore the structure and composition of the UFe/PS core–shell composite microspheres and the UFe–PMPS Janus composite particles. Results showed that UFe/PS core–shell composite microspheres with different thickness of UFe shell could be obtained by adjusting the sulfonated time. After UFe/PS with appropriate thickness of UFe shell swelled with MPS and was polymerized, dumbbell-like UFe–PMPS Janus composite particles were prepared successfully. The UFe–PMPS Janus composite particles were compartmentalized two parts with different morphology. The anisotropic Janus composite particles of UFe–PMPS will be expected to have application in functional materials or oriental coatings.

1. Introduction

Raw lacquer is a quality natural paint. Due to its excellent physico-mechanical properties and high durability, the research of raw lacquer for usage as organic coatings has attracted great interest over the last several millennia [1,2]. Recently, studies on the renewable resources of raw lacquer were focusing on its modification [3,4], and the methods to solve the problems of slow drying and coating difficultly [5–7]. The main component of raw lacquer is urushiol () which is a o-dihydroxybenzene containing an unsaturated side chain [8]. The two adjacent phenolic hydroxyls of urushiol can react with metal compounds and obtain urushiol-metal chelate polymer [8–11]. By this way, the functionalization of urushiol is catching the eyes of researchers. Owing to the special chemical structure, urushiol-metal chelate polymer has superior properties in heat resistance, acid–alkaline resistance and catalysis [9,12].

Since the speech of the Nobel laureates de Gennes in 1991, the research on Janus composite particles has been a hot area in materials science [13–16]. Janus composite particles are fabricated as two parts with different morphology or surface chemical properties [17,18]. Janus composite particles with anisotropy show great promising application in micro-reactor [19], compatibility agents [20], solid surfactants [21], catalysts [22], etc. Therefore, it is of great theoretical and realistic significance to synthesize novel morphological and anisotropic Janus material. To date, there are numerous methods that have been developed to prepare Janus composite particles. Among these, the method of emulsion swelling assisted protrusion arouses extensive interest of researchers because of its batch production and controllable morphology [23–25].

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http://dx.doi.org/10.1016/j.porgcoat.2014.09.023
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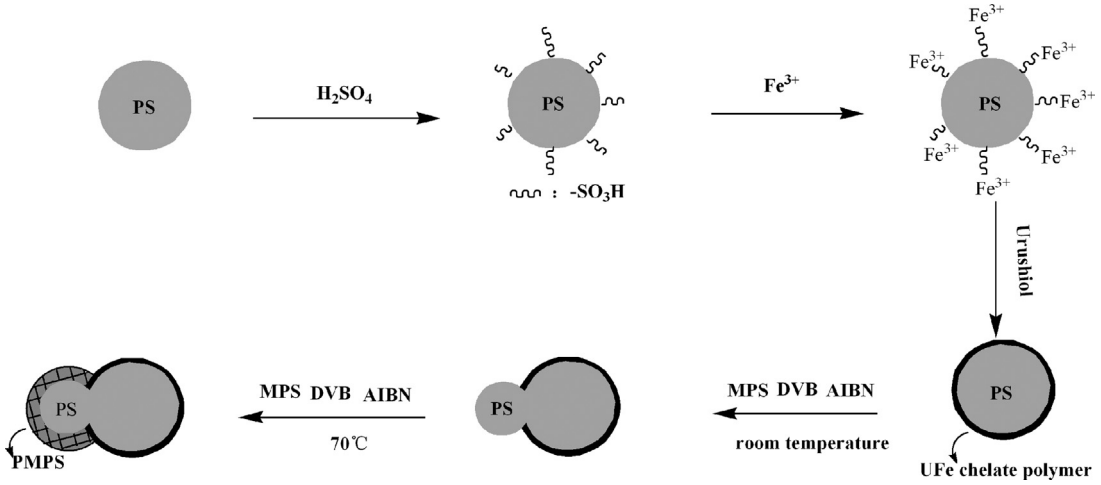

Scheme 1. The preparation of UFe–PMPS Janus composite particles.

To the best of our knowledge, there have been very few studies on the preparation of urushiol-metal chelate polymer for Janus composite particles. In our previous work, the Janus composite particles of urushiol-titanium chelate polymer (UTi)/polystyrene (PS) have been synthesized successfully [8]. In order to further expand the application of raw lacquer, preparation of its functional material is a challenging and interesting work. Thus, it is very interesting to introduce the anisotropic Janus composite particles based on urushiol-iron/polystyrene polymer. In this paper, Fe^{3+} was adsorbed on the surface of the sulfonated polystyrene (SPS) microspheres, and then the reaction between Fe^{3+} and urushiol occurred and formed the UFe/PS core–shell composite microspheres. After that the shell thickness of UFe coated on the surface of SPS was tunable. Finally, the Janus particles of UFe–poly (2-propenoic acid, 2-methyl-, 3-(trimethoxysilyl) propyl ester) (PMPS) were obtained by the method of emulsion swelling assisted protrusion. The anisotropic Janus composite particles of UFe–PMPS will be expected to have application in functional materials or oriental coatings.

2. Experimental

2.1. Materials

Chinese lacquer was purchased from the Institute of Lacquer, Xi'an, China. Urushiol was extracted with acetone from Chinese lacquer. Styrene (St), ethanol, ferric chloride ($FeCl_3$), concentrated sulfuric acid, 2-propenoic acid, 2-methyl-, 3-(trimethoxysilyl) propyl ester (MPS), 2,2-azobisisobutyronitrile (AIBN), Divinylbenzene (DVB) and sodium dodecyl benzene sulfonate (SDBS) were purchased from Sinopharm Chemical Reagent Co., Ltd. St, MPS and DVB were used after purification with alkaline Al_2O_3 to remove the inhibitor.

2.2. Synthesis of the core–shell composite microspheres of UFe/PS

The sulfonated polystyrene (SPS) microspheres were prepared according to the reported literatures [26,27]. The mixture of SPS and 1% $FeCl_3$ was stirred at the room temperature for more than 8 h to allow a saturated adsorption of Fe^{3+}. After removing the excess Fe^{3+}, the urushiol dispersed in ethanol was added under stirring at room temperature for 4 h. The UFe/PS core–shell composite microspheres were obtained after centrifugation and washing with ethanol.

2.3. Synthesis of the Janus composite particles of UFe–PMPS

A certain amount of MPS, DVB, AIBN and SDBS mixed emulsion was added to the dispersion of UFe/PS composite microspheres in a flask under stirring at room temperature for 20 min. Then, the flask was transferred into the water bath at 70 °C for more than 10 h under stirring. The UFe–PMPS Janus composite particles were achieved after being washed and dried.

2.4. Characterization

The morphology of the samples was characterized by a JSM-7500F scanning electron microscope (SEM) with operation voltage of 5 kV. The chemical composition was analyzed by an Oxford

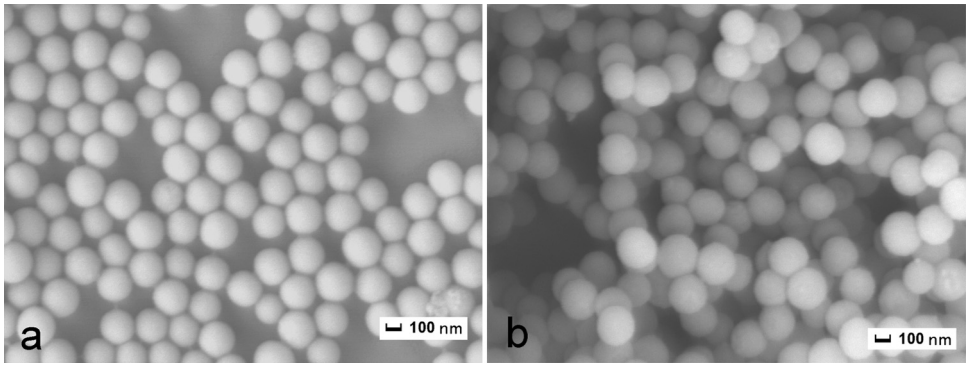

Fig. 1. SEM images of (a) PS microspheres and (b) UFe/PS core–shell composite microspheres.